Two-Dimensional Electronic States of Random Alloy Surfaces

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Despite their enormous importance in technological applications, relatively little experimental work regarding the details of the electronic states in random alloys has been done to date. Although the complete translational periodicity has in principle been lost, in fact the surfaces of such alloys can yield very sharp low energy diffraction patterns. Therefore, one might expect that surface electronic states of similar quality to perfectly ordered crystalline surfaces might be obtained.

We chose to measure surface states for $Mo_{1-x}Re_x(110)$ because it has been well-demonstrated that these alloys are random, i.e. there is no local compositional ordering. Furthermore, the stoichiometry has been found to be maintained up to the surface layers[1]. The pure Mo surface states are well-characterized from previous work, both for clean and hydrogen-covered preparations.[2] In this work, the surfaces have been saturated with hydrogen in order to enhance the surface spin-orbit interaction to be discussed below.

Photoemission experiments were conducted at the permanent photoemission endstation at beamline 7.0 of the Advanced Light Sources. Crystals were prepared in situ by annealing in oxygen at 1150C and flash-annealling to ~2100C. The stoichiometry of the crystals was deterimed *ex situ* by ion scattering and confirmed for in situ prepared surfaces using Mg Ka x-rays core level photoemission. The base pressure of the system was 8 x 10^{-11} T. The experiments were conducted at a sample temperature of ~130K. Further details on the experimental setup are provided elsewhere.[3]

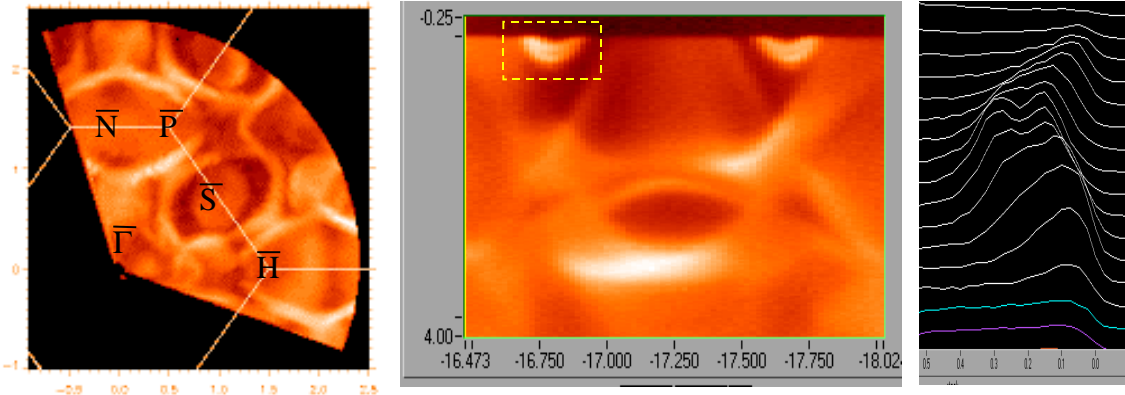Figure 1 shows typical photoemission data for 1 monolayer H on pure Mo(110).

Figure 1. Angle-resolved photoemission for 1 ML H on Mo(110). (a) Constant energy map vs $k_{||}$ for electrons at the Fermi level E_F. The bright features correspond to electronic bands crossing the Fermi level. (b) Intensity map of the valence band density of states taken along the line P-H of the surface Brillouin zone. (c) Individual spectra for the region within the dashed box of (b). The splitting due to spin-orbit interaction is clearly visible.

In figure 1(a) we show the measured density of states at the Fermi level E_F for momenta in the $\mathbf{k}_\parallel$-plane. There are ellipsoidal contours centered on the N and S points of the surface Brillouin zone (SBZ). These features are very similar to those reported for H on W, and Li on Mo, except that their exact dimensions are different in the H on Mo case presented here. Figure 1(b) shows valence band spectra along P to H of the SBZ, and it becomes clear that these ellipsoidal Fermi contours are hole pockets, and that the orbits surrounding N and S points are in fact connected at binding energies below E_F.

Further consideration of these spectra show that the bands underlying the Fermi contours are in fact split. Although the steepness of the bands and the limited angular sampling conspire to make the splitting unresolved in figure 1(a), it is most clearly obvious at the bottom of the bands in figure 1(b). This is demonstrated in figure 1(c), which shows individual spectra from the dashed region in figure 1(b). We attribute the splitting to the spin-orbit coupling effect, which has previously been found in clean Au(111)[4] and for H and Li on W(110).[5] That the splitting is at all apparent given our experimental resolution is due to the fact that the sample is H-saturated. As shown in ref [5] the splitting increases as a function of hydrogen coverage both because of the change in surface electric field gradient as well as the increased degree of localization of the surface state to the surface layers attendant upon hydrogen adsorption.

Next we ask, what happens when the pure Mo crystal is alloyed with Re? Figure 2 shows a series of bandmaps for 5%, 15%, and 25% Re compositions. It is clear that there is a tendency for the overall bandwidths to systematically increase, which we have also found for the bulk bands in this system.[6] There are two contributing factors to the increase in bandwidth. First, since the valences of Re and Mo are d^5s^2 and d^5s^1, respectively, it might be expected that the extra Re electron act as a dopant electron. This could, depending on the degree of d-s hybridization, effectively increase the population of the d-derived surface states we study, thus raising the Fermi level for these bands. To the extent that this is true would be confirmation of the so-called rigid-band model for alloy electronic states.[6] The second reason is an additional well-known relativistic effect which uniformly widens the bands in third row elements compared to second row: as the mass of the s-electrons increases, drawing the s-orbitals closer to the core, the resulting increased screening of the core causes the d-orbitals to expand outwards. This results in a uniform widening of the d-bands due to more d-d overlap between adjacent atoms.
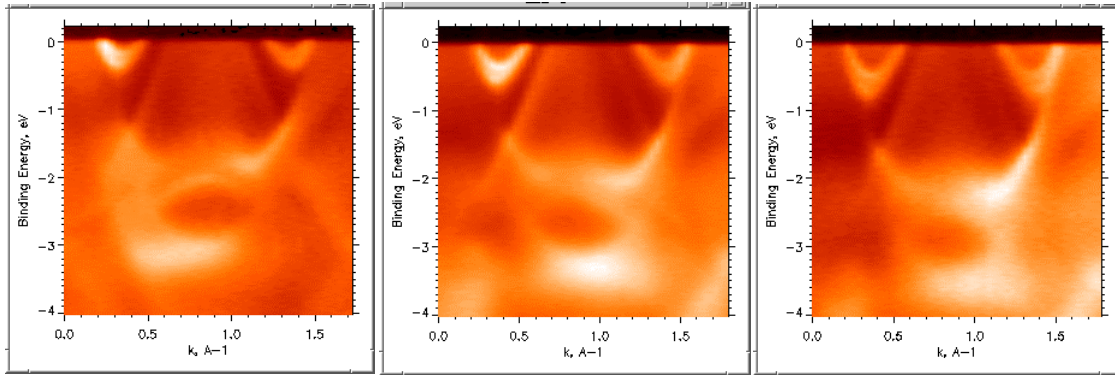

Figure 2. Valence Band Intensity maps along P-H in the surface Brioullin Zone for $Mo_{1-x}Re_x$ for (a) x=0.05, (b) x=0.15, (c) x=0.25.

More importantly for this work, there is an obvious tendency for the spin-orbit splitting to increase with Re content. This increased splitting is the most important feature of this work because being due to relativistic effect, it can only arise from electronic overlap with a small region near the increased mass at the center of the Re muffin tin potential. Figure 3 shows the trend of this splitting vs. Re content. The splitting follows a nearly linear increase with Re coverage. Extrapolating the splitting to what we would get for pure Re (provided that pure Re would crystallize as bcc) we predict a splitting of ~0.5 eV, which is very close to the value for bcc W in the same region of k-space.[7] That the increase is linear suggests that the surface state wavefunction is sampling Mo and Re with equal probability per atom.

To conclude, we have shown that alloying a surface layer with a relativistically heavy atom induces a measurable change in the spin-orbit splitting of the surface electronic states, without fundamentally altering the character of the states. Since this
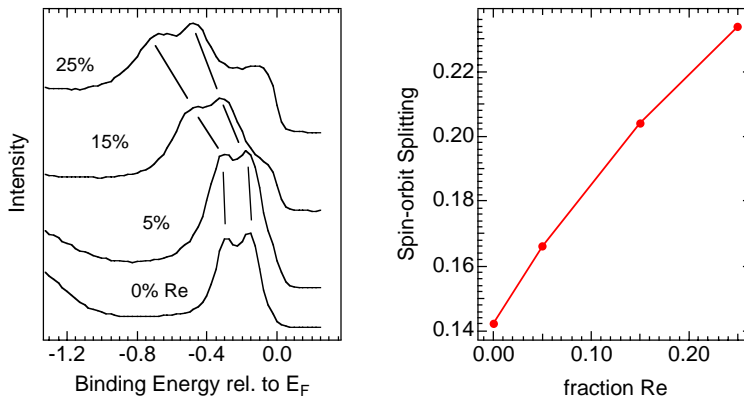

Figure 3. Spin-orbit splitting as a function of Re content. (left) spectra taken at the bottom of the bands along P-H, showing the maximum splitting. (right) the splitting derived from quantitative curve-fitting of these data as a function of coverage.

splitting is also sensitive to local surface potentials, overlayer growth of heavier transition metals on first row magnetic transition metals, especially at step edges, might serve as a useful probe of surface spin-orbit coupling at these surfaces. This could prove a useful tool to understand the origins of magnetic anisotropy and coupling at magnetic multilayer interfaces.

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